Chapter 4
Background Theory

In this chapter, we briefly introduce the quantum confinement for different geometries and the formalism of the Fermi's Golden Rule. More details can be found in any quantum mechanics book, e.g., Refs. [1, 2].

4.1 Quantum Cofinement

4.1.1 Three Dimensional Cartesian Coordinates

The time-dependent Schrödinger equation for a spinless particle of mass m moving under the influence of a three-dimensional potential is

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\Psi(x,y,z,t)+\hat{V}(x,y,z,t)\Psi(x,y,z,t)=i\hbar\frac{\partial\Psi(x,y,z,t)}{\partial t} \tag{4.1}$$

where $\vec{\nabla}$ is the Laplacian given by

$$\vec{\nabla}^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2} \tag{4.2}$$

The wavefunction of a particle in a time-independent potential can be written as a product of spatial and time components:

$$\Psi(x,y,z,t)=\psi(x,y,z)e^{-i\frac{Et}{\hbar}} \tag{4.3}$$

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where $\psi(x, y, z)$ is the solution to the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi(x, y, z) + \hat{V}(x, y, z)\psi(x, y, z) = E\psi(x, y, z) \tag{4.4}$$

which is of the from $\hat{H}\psi = E\psi$. If the potential can be separated into the sum of three independent, one-dimensional terms

$$V(x, y, z) = V(x) + V(y) + V(z) \tag{4.5}$$

we can solve (4.4) by the method of *separation of variables*. This method consists of separating the three-dimensional Schrödinger equation into three independent one-dimensional Schrödinger equations. Then (4.4), in conjugation with (4.5), can be written as

$$\left[\hat{H}_x + \hat{H}_y + \hat{H}_z\right]\psi(x, y, z) = E\psi(x, y, z) \tag{4.6}$$

where $\hat{H}_\alpha$ is given by

$$H_\alpha = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\alpha^2} + V_\alpha(\alpha) \tag{4.7}$$

with $\alpha = x, y, z$.

As $V(x, y, z)$ separates into three independent terms, we can also write $\psi(x, y, z)$ as a product of three functions, each with a single variable:

$$\psi(x, y, z) = X(x)Y(y)Z(z) \tag{4.8}$$

Substituting (4.8) into (4.6) and dividing it by $X(x)Y(y)Z(z)$, we obtain

$$\left[-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2} + V_x(x)\right] + \left[-\frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2Y}{dy^2} + V_y(y)\right] + \left[-\frac{\hbar^2}{2m}\frac{1}{Z}\frac{d^2Z}{dz^2} + V_z(z)\right] = E \tag{4.9}$$

Since each expression in the square brackets depends on only one of the variables x, y, or z, and since the sum of these three expressions is equal to a constant energy, E, each expression must then be equal to a constant such that the sum of these three constants is equal to E. For instant, the x-dependent expression is given by

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_x(x)\right]X(x) = E_xX(x) \tag{4.10}$$

Similar equations are also applicable for the y and z coordinates, with

$$E_x + E_y + E_z = E \tag{4.11}$$

4.1.2 The Box Potential

We begin with the rectangular box potential, which has no symmetry, and then consider the cubic potential, which displays a great deal of symmetry, since x, y, and z axes are equivalent.

4.1.2.1 The Rectangular Box Potential

Consider first the case of a spinless particle of mass m confined in a *rectangular* box of sides L_x, L_y and L_z:

$$V(x,y,z) = \begin{cases} 0 & \text{if } 0<x<L_x, 0<y<L_y, 0<z<L_z \\ \infty & \text{elsewhere} \end{cases} \tag{4.12}$$

which can be written as $V(x,y,z) = V_x(x) + V_y(y) + V_z(z)$, with

$$V_x(x) = \begin{cases} 0 & \text{if } 0<x<L_x \\ \infty & \text{elsewhere} \end{cases} \tag{4.13}$$

and the potential $V_y(y)$ and $V_z(z)$ have similar forms.

The wavefunction $\psi(x,y,z)$ must vanish at the walls of the box. The solutions for this potential are of the form

$$X(x) = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n_x \pi}{L_x} x\right) \quad n_x = 1, 2, 3, \ldots \tag{4.14}$$

and the corresponding energy eigenvalues are

$$E_{n_x} = \frac{\hbar^2 \pi^2}{2mL_x^2} n_x^2 \tag{4.15}$$

From these expressions we can write the normalized three-dimensional eigenfunctions and their corresponding energies:

$$\psi_{n_x n_y n_z}(x,y,z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi}{L_x} x\right) \sin\left(\frac{n_y \pi}{L_y} y\right) \sin\left(\frac{n_z \pi}{L_z} z\right) \tag{4.16}$$

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \tag{4.17}$$

where $n_x, n_y, n_z = 1, 2, 3, \ldots$.

4.1.2.2 The Cubic Box Potential

Similarly to the previous case, we consider the case of a spinless particle of mass m confined in a *cubic* box of side L.

$$V(x, y, z) = \begin{cases} 0 & \text{if } 0 < x < L,\ 0 < y < L,\ 0 < z < L \\ \infty & \text{elsewhere} \end{cases} \tag{4.18}$$

Recalling the results obtained for the rectangular case, (4.16) and (4.17), the eigenfunctions and eigenenergies are:

$$\psi_{n_x n_y n_z}(x, y, z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right) \tag{4.19}$$

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right) \tag{4.20}$$

The ground state, $n_x = n_y = n_z = 1$, has energy

$$E_{111} = \frac{3\hbar^2 \pi^2}{2mL^2} \tag{4.21}$$

There is three first excited states, corresponding to the three combination of n_x, n_y and n_z, i.e., $n_x = 2$, $n_y = 1$, $n_z = 1$, or $n_x = 1$, $n_y = 2$, $n_z = 1$ or $n_x = 1$, $n_y = 1$, $n_z = 2$ whose squares sum to 6. The first excited state has energy

$$E_{211} = E_{121} = E_{112} = \frac{6\hbar^2 \pi^2}{2mL^2} \tag{4.22}$$

Note that each of the first excited states is characterized by different wavefunction: ψ_{211} has wavelength L along the x-axes and wavelength $2L$ along the y- and z-axes, but for ψ_{121} and ψ_{121} the shorter wavelength is along the y-axis and the z-axis, respectively.

Whenever different states have the same energy, this energy level is said to be *degenerate*. In the case above, the first excited level is three-fold degenerate. This system has degenerate levels because of the high degree of symmetry associated with the cubic shape of the box. The degeneracy would be lifted, if the sides of the box were of unequal lengths (rectangular box).

4.1.3 Three Dimensional Spherical Coordinates

In this section, we study the structure of the Schrödinger equation for a particle of mass M moving in a spherically symmetric potential

$$V(\mathbf{r}) = V(r) \tag{4.23}$$

which is also known as the *central* potential.

The time-independent Schrödinger equation for a particle of momentum $-i\hbar\nabla$ and the potential vector $\mathbf{r}$ is

$$\left[-\frac{\hbar^2}{2M}\nabla^2 + V(r)\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{4.24}$$

The Laplacian ∇_r^2 separates into a radial part and an angular part ∇_Ω^2 as follows

$$\nabla^2 = \nabla_r^2 + \frac{1}{\hbar^2 r^2}\nabla_\Omega^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{\hbar^2 r^2}\hat{\mathbf{L}}^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{1}{\hbar^2 r^2}\hat{\mathbf{L}}^2 \tag{4.25}$$

where $\hat{\mathbf{L}}$ is the orbital angular momentum

$$\hat{\mathbf{L}}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] \tag{4.26}$$

In spherical coordinates, the Schrödinger takes the form of

$$\left[-\frac{\hbar^2}{2M}\frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{1}{2Mr^2}\hat{\mathbf{L}}^2 + V(r)\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{4.27}$$

The first term of this equation can be viewed as the radial kinetic energy

$$-\frac{\hbar^2}{2M}\frac{1}{r}\frac{\partial^2}{\partial r^2}r = \frac{\hat{\mathbf{P}}_r^2}{2M} \tag{4.28}$$

since the radial momentum operator is given in the Hermitian form

$$\hat{\mathbf{P}}_r = \frac{1}{2}\left[\left(\frac{\mathbf{r}}{r}\right)\cdot\hat{\mathbf{P}} + \hat{\mathbf{P}}\cdot\left(\frac{\mathbf{r}}{r}\right)\right] = i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) \equiv -i\hbar\frac{1}{r}\frac{\partial}{\partial r}r \tag{4.29}$$

The second term $\mathbf{L}^2/(2Mr^2)$ can be identified with the rotational kinetic energy because it is generated from the pure rotation of the particle about the origin with

the momentum of inertia with respect to the origin of Mr^2. In addition, $\hat{\mathbf{L}}^2$ commute with $\hat{\mathbf{L}}_z$ and $\hat{\mathbf{H}}$ as follows

$$\left[\hat{\mathbf{H}}, \hat{\mathbf{L}}^2\right] = \left[\hat{\mathbf{H}}, \hat{\mathbf{L}}_z\right] = 0 \tag{4.30}$$

Thus $\hat{\mathbf{H}}$, $\hat{\mathbf{L}}^2$, and $\hat{\mathbf{L}}_z$ have common eigenfunctions. The simultaneous eigenfunction of $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{L}}_z$ are given by the spherical harmonics

$$\hat{\mathbf{L}}^2 Y_{lm}(\theta, \varphi) = l(l+1)\hbar^2 Y_{lm}(\theta, \varphi) \tag{4.31}$$

$$\hat{\mathbf{L}}_z Y_{lm}(\theta, \varphi) = m\hbar Y_{lm}(\theta, \varphi) \tag{4.32}$$

The Hamiltonian in (4.27) is a sum of a radial part and an angular part. Thus, we can look for solutions that are products of a radial part and an angular part

$$\psi(\mathbf{r}) = \langle r \mid nlm \rangle = \psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) Y_{lm}(\theta, \varphi) \tag{4.33}$$

The radial wavefunction $R_{nl}(r)$ has to be found. The quantum number n is introduced to identify the eigenvalues of $\hat{\mathbf{H}}$:

$$\hat{\mathbf{H}}|nlm\rangle = E_n|nlm\rangle \tag{4.34}$$

Substituting (4.34) into (4.27) and using the fact that $\psi_{nlm}(r, \theta, \varphi)$ is an eigenfunction of $\hat{\mathbf{L}}^2$ (4.31), then dividing by $R_{nl}(r)Y_{lm}(\theta, \varphi)$ and multiplying by $2Mr^2$, we obtain an expression where the radial and angular degrees of freedom are separated into

$$\begin{gathered}
\left[-\hbar^2 \frac{r}{R_{nl}} \frac{\partial^2}{\partial r^2}(rR_{nl}) + 2Mr^2(V(r) - E)\right] + \left[\frac{\hat{\mathbf{L}}^2 Y_{lm}(\theta, \varphi)}{Y_{lm}(\theta, \varphi)}\right] = 0 \\
\left[-\hbar^2 \frac{r}{R_{nl}} \frac{\partial^2}{\partial r^2}(rR_{nl}) + 2Mr^2(V(r) - E)\right] + \left[\frac{l(l+1)\hbar^2 Y_{lm}(\theta, \varphi)}{Y_{lm}(\theta, \varphi)}\right] = 0 \\
\left[-\hbar^2 \frac{r}{R_{nl}} \frac{\partial^2}{\partial r^2}(rR_{nl}) + 2Mr^2(V(r) - E)\right] + \left[l(l+1)\hbar^2\right] = 0
\end{gathered} \tag{4.35}$$

The last expression only depends on r and the final expression is thus simplified as

$$-\frac{\hbar^2}{2M}\frac{d^2}{dr^2}(rR_{nl}(r)) + \left[V(r) + \frac{l(l+1)\hbar^2}{2Mr^2}\right](rR_{nl}(r)) = E_n(rR_{nl}(r)) \tag{4.36}$$

Note that (4.36) does not depend on the azimuthal quantum number m. Thus, the energy E_n is $2l(l+1)$—fold *degenerate*. This is due to the fact that, for a given l, there are $(2l+1)$ different eigenfunctions ψ_{nlm} (i.e., $\psi_{nl\,-l}$, $\psi_{nl\,-l+1}$, …, $\psi_{nl\,l-1}$, $\psi_{nl\,l}$), which correspond to the same eigenenergy E_n. This degeneracy property is peculiar to the central potentials. Moreover, (4.36) has the structure of a one-dimensional equation for r as follows

$$-\frac{\hbar^2}{2M}\frac{d^2U_{nl}(r)}{dr^2}+V_{eff}(r)U_{nl}(r)=E_nU_{nl}(r) \tag{4.37}$$

whose solutions give the energy levels of the system with the wavefunction given by

$$U_{nl}(r)=rR_{nl}(r) \tag{4.38}$$

and the potential by

$$V_{eff}(r)=V(r)+\frac{l(l+1)\hbar^2}{2Mr^2} \tag{4.39}$$

which is known as the *effective* or *centrifugal* potential. Here, $V(r)$ is the central potential and $l(l+1)\hbar^2/(2Mr^2)$ is a repulsive or centrifugal potential, which is associated with the orbital angular momentum and tends to repel the particle away from the center. $\psi_{nlm}(r,\theta,\varphi)$ is finite for all values of r spanning from 0 to ∞. Thus, if $R_{nl}(0)$ is finite, $rR_{nl}(r)$ must vanish at $r = 0$, i.e.,

$$\lim_{r\to 0}[rR_{nl}(r)]=U_{nl}(0)=0 \tag{4.40}$$

4.1.3.1 Free Particle in Spherical Coordinates

Here, we apply the formalism developed above to study the motion of a free particle of mass M and energy $E_k=\hbar^2k^2/(2M)$ where k is the wave vector $k=|\mathbf{k}|$. The Hamiltonian $H=-\hbar^2\nabla^2/(2M)$ of a free particle is *rotational invariant* and commutes with $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{L}}_z$. Thus, the radial equation for a free particle is

$$-\frac{\hbar^2}{2M}\frac{1}{r}\frac{d^2}{dr^2}(rR_{kl}(r))+\frac{l(l+1)}{2Mr^2}R_{kl}(r)=ER_{kl}(r) \tag{4.41}$$

using a change of variable $\rho=kr$, we reduce this equation into

$$\frac{d^2R_l(\rho)}{d\rho^2}+\frac{2}{\rho}\frac{dR_l(\rho)}{d\rho}+\left[1-\frac{l(l+1)}{\rho^2}\right]R_l(\rho)=0 \tag{4.42}$$

where $R_l(\rho) = R_l(kr) = R_{kl}(r)$. This differential equation is known as the *spherical Bessel* equation. The general solutions to this equation are given by the spherical Bessel functions $j_l(\rho)$ and the spherical Neumann functions $n_l(\rho)$. Since the Neumann functions $n_l(\rho)$ diverge at the origin, and since the wavefunctions $\psi_{klm}(r, \theta, \varphi)$ are required to be finite everywhere in space, only the spherical Bessel functions $j_l(\rho)$ contribute to the eigenfunctions of the free particle

$$\psi_{klm}(r, \theta, \varphi) = j_l(kr) Y_{lm}(\theta, \varphi) \tag{4.43}$$

where $k = \sqrt{2ME_k}/\hbar$. Note that, since the index k in $E_k = \hbar^2 k^2/(2M)$ varies *continuously*, the energy spectrum of a free particle is *infinitely degenerate*. This is because all orientations of **k** in space correspond to the same energy.

4.1.3.2 The Spherical Well

We consider a particle of mass M confined to the interior of a spherical well with impenetrable walls. In the domain $r \geq a$, the wavefunction vanishes. In the domain $r < a$, the potential is zero.

$$V(r) = \begin{cases} 0 & \text{if } r < a \\ \infty & \text{if } r \geq a \end{cases} \tag{4.44}$$

To impose the boundary condition $\psi(r = a) = 0$, we set

$$j_l(ka) = j_l(x) = j_l(x_{nl}) = 0 \tag{4.45}$$

where $x \equiv ka$ and x_{nl} is the nth zero of $j_l(x)$. Thus, the eigenfunctions and eigenvalues for the spherical well are given by nth

$$\psi_{nlm}(r, \theta, \varphi) = j_l\left(\frac{x_{nl}}{a} r\right) Y_{lm}(\theta, \varphi) \tag{4.46}$$

$$E_{nl} = \frac{\hbar^2 x_{nl}^2}{2Ma^2} \tag{4.47}$$

4.1.4 Three Dimensional Cylindrical Coordinates

We next consider the case of a particle of mass M confined to a cylindrical box of radius a and length L; that is,

$$V(r, \phi, z) = \begin{cases} 0 & r < a \quad 0 < z < L \\ \infty & \text{elsewhere} \end{cases} \tag{4.48}$$

Employing the Hamiltonian in cylindrical coordinates, the Schrödinger equation for the confined particle is given by

$$\frac{\partial^2\psi}{\partial r^2}+\frac{1}{r}\frac{\partial\psi}{\partial r}+\frac{1}{r^2}\frac{\partial^2\psi}{\partial\phi^2}+\frac{\partial^2\psi}{\partial z^2}+k^2\psi=0 \tag{4.49}$$

$$E=\frac{\hbar^2k^2}{2M} \tag{4.50}$$

with the separation of coordinates

$$\psi(r,\phi,z)=R(r)\Phi(\phi)Z(z) \tag{4.51}$$

Eq. (4.49) becomes

$$\frac{1}{R}\left(\frac{\partial^2R}{\partial r^2}+\frac{1}{r}\frac{\partial R}{\partial r}\right)+\frac{1}{r^2}\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}+\frac{1}{Z}\frac{\partial^2Z}{\partial z^2}+k^2=0 \tag{4.52}$$

It follows that

$$\frac{1}{Z}\frac{\partial^2Z}{\partial z^2}=\text{constant}\equiv-k_z^2 \tag{4.53}$$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=\text{constant}=-m^2 \tag{4.54}$$

$$\frac{1}{R}\left(r^2\frac{\partial^2R}{\partial r^2}+r\frac{\partial R}{\partial r}\right)+r^2\left(k^2-k_z^2\right)=m^2 \tag{4.55}$$

Applying boundary conditions (4.48), we find

$$Z(z)=A\sin(k_zz);k_zL=n_z\pi;n_z=1,2,\ldots \tag{4.56}$$

Furthermore, as $\Phi(\phi)=\Phi(\phi+2\pi)$, we obtain

$$\Phi(\phi)=Be^{im\phi};m=0,\pm1,\pm2,\ldots \tag{4.57}$$

where A and B are constant. Returning to (4.55) and labelling

$$k^2-k_z^2\equiv K^2 \tag{4.58}$$

$$\rho\equiv Kr \tag{4.59}$$

There results

$$\rho^2 \frac{d^2R}{d\rho^2} + \rho \frac{dR}{d\rho} + \left(\rho^2 - m^2\right)R = 0 \tag{4.60}$$

which is known as *Bessel's equation*. General solution to this equation are given by

$$R(\rho) = C_1 J_m(\rho) + C_2 N_m(\rho) \tag{4.61}$$

where C_1 and C_2 are constants. The functions $J_m(\rho)$ and $N_m(\rho)$ are called *Bessel* and *Neumann functions of the first kind*, respectively. Since $N_m(0) = -\infty$, the only acceptable solution for the wavefunction are $J_m(\rho)$. The remaining boundary conditions gives

$$R(r = a) = C_1 J_m(aK) = 0 \tag{4.62}$$

Let us call the sth finite zero of $J_m(\rho), x_{ms}$ so that

$$J_m(aK_{ms}) \equiv J_m(x_{ms}) = 0 \tag{4.63}$$

Thus, the eigenfunctions are given by

$$\psi_{msn_z}(r, \phi, z) = AJ_m\left(\frac{x_{mx}}{a} r\right) \sin\left(\frac{n_z \pi}{L} z\right) e^{im\phi} \tag{4.64}$$

with $m \geq 0$, $s > 0$, $n_z \geq 1$, and all three parameters are integers. The corresponding eigenenergies are

$$E = \frac{\hbar^2 k^2}{2M} = \frac{\hbar^2}{2M}\left(K^2 + k_z^2\right) = \frac{\hbar^2}{2M}\left[K_{ms}^2 + \left(\frac{n_z \pi}{L}\right)^2\right] \tag{4.65}$$

with $x_{ms} = aK_{ms}$, the former becomes

$$E_{msn_z} = \frac{\hbar^2}{2M}\left[\frac{x_{ms}^2}{a^2} + \left(\frac{n_z \pi}{L}\right)^2\right] \tag{4.66}$$

4.2 Fermi's Golden Rule

The transition probability corresponding to a transition from an initial unperturbed state $|\psi_i\rangle$ to another unperturbed state $|\psi_f\rangle$ is

$$P_{if}(t) = \left| -\frac{i}{\hbar} \int_0^t \langle \psi_f | \hat{V}(t') | \psi_i \rangle e^{i\omega_{fi} t'} dt' \right|^2 \tag{4.67}$$

In the case where $\hat{V}$ does not depend on time, (4.67) reduces to

$$P_{if}(t) = \left|\langle\psi_f|\hat{V}|\psi_i\rangle\right|^2 \frac{\sin^2\left(\frac{1}{2}\hbar\omega_{fi}t\right)}{\left(\frac{1}{2}\hbar\omega_{fi}\right)^2} \tag{4.68}$$

As a function of the time, this transition probability is an oscillating sinusoidal function with a period of $2\pi/\omega_{fi}$. As a function of ω_{fi}, the transition probability, as shown in (4.68), has an interference pattern: it is appreciable only near $\omega_{fi} \simeq 0$ and decays rapidly as ω_{fi} moves away from zero (Fig. 4.1). Hence, for a fix t, we have assumed that ω_{fi} is a continuous variable; that is, we have considered a continuum of final states. This means that the transition probability of finding the system in a state $|\psi_f\rangle$ of energy E_f is the greatest only when $\omega_{fi} \simeq 0$ or equivalently when $E_i \simeq E_f$. The height and the width of the main peak, centered around $\omega_{fi} = 0$, are proportional to t^2 and $1/t$, respectively. Therefore, the area under the probability curve is proportional to t. Since most of the area is under the central peak, the transition probability is proportional to t. Therefore, the transition probability grows linearly with time. The central peak becomes narrower and stronger as time increases; this is exactly the property of a delta function. Thus, in the limit $t \to \infty$, the transition probability takes the shape of a delta function. Therefore, (4.68) boils down to

$$P_{if}(t) = \frac{2\pi t}{\hbar}\left|\langle\psi_f|\hat{V}|\psi_i\rangle\right|^2 \delta(E_f - E_i) \tag{4.69}$$

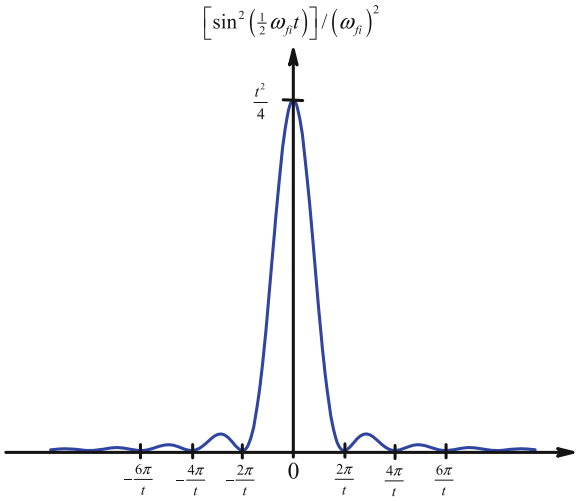

Fig. 4.1 $\left[\sin^2\left(\frac{1}{2}\omega_{fi}t\right)\right]/\left(\omega_{fi}\right)^2$ versus ω_{fi} for a fixed value of t when $\omega_{fi} = (E_f - E_i)/2$

To obtain (4.69), we use the following properties:

$$\frac{\sin^2\left(\frac{1}{2}\omega_{fi}t\right)}{\left(\frac{1}{2}\omega_{fi}\right)^2} = 2\pi t\hbar\delta\left(\hbar\omega_{fi}\right) \tag{4.70}$$

$$\hbar\omega_{fi} = E_f - E_i \tag{4.71}$$

The *transition rate*, which is defined as the transition probability per unit time, is given by

$$\Gamma_{if} = \frac{P_{if}(t)}{t} = \frac{2\pi}{\hbar}\left|\langle\psi_f|\hat{V}|\psi_i\rangle\right|^2\delta\left(E_f - E_i\right) \tag{4.72}$$

The delta term $\delta\left(E_f - E_i\right)$ guarantees the conservation of energy: in the limit $t \to \infty$, the transition rate is nonvanishing only between the states of equal energy. Hence, a constant perturbation neither removes energy from the system nor supplies energy to it.

Let us now calculate the total transition rate associated with a transition from an initial state $|\psi_i\rangle$ into a continuum of final states $|\psi_f\rangle$. If $\rho\left(E_f\right)$ is the density of final states—the number of states per unit energy intervals—the number of final states within the energy intervals E_f and $E_f + dE_f$ is equal to $\rho\left(E_f\right)dE_f$. Then, the total transition rate W_{if} can be obtained from (4.72):

$$W_{if} = \int \frac{P_{if}(t)}{t}\rho\left(E_f\right)dE_f = \frac{2\pi}{\hbar}\left|\langle\psi_f|\hat{V}|\psi_i\rangle\right|^2\int \rho\left(E_f\right)\delta\left(E_f - E_i\right)dE_f \tag{4.73}$$

$$W_{if} = \frac{2\pi}{\hbar}\left|\langle\psi_f|\hat{V}|\psi_i\rangle\right|^2\rho(E_i) \tag{4.74}$$

This relation is called the *Fermi's Golden Rule*. It implies that, in the case of a constant perturbation, if we wait long enough, the total transition rate becomes constant.

References

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